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STUDY OF PHYSICAL AND MECHANICAL PROPERTIES OF DIFFUSION LAYERS OBTAINED USING COMPOSITE SATURATIVE ENVIRONMENTS

Multicomponent diffusion saturation can increase the hardness and wear resistance, heat resistance and corrosion resistance of metals and alloys in various environments, due to the formation of phases of a complex composition and structure in the surface layer. The physicomechanical properties of diffusion layers obtained using composite saturating media are investigated.

Surface saturation of alloys simultaneously with two elements has an advantage over saturation with one element. It allows you to combine in the resulting coating the properties created by individual elements with the special properties of their compounds. Due to the fact that the elements that make up the saturating mixture have different diffusion coefficients in the alloy, and also have a mutual influence on the diffusion rate of each other, the choice of the composition of the charge in a complex process is a difficult task.

On the results, we can say mechanical stresses (in this case, the compressive residual stresses) affect the corrosion behavior of metals, due to the extraction of the structural material by the fact that the level of residual stresses in coatings obtained under composite saturating environments charge is higher. As a result, the probability of micro-bursting of passive oxide skins is reduced, resulting in an increase in corrosion resistance.

Key words: composite saturating environment, brass, diffusion, diffusion layers, titanium, aluminum, silicon, chromium.

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ДОСЛІДЖЕННЯ ФІЗИКО-МЕХАНІЧНИХ ВЛАСТИВОСТЕЙ ДИФУЗІЙНИХ ШАРІВ, ОТРИМАНИХ З ВИКОРИСТАННЯМ КОМПОЗИЦІЙНИХ НАСИЧУЮЧИХ СЕРЕДОВИЩ

Багатокомпонентним дифузійним насиченням можна підвищити твердість і зносостійкість, жаростійкість і корозійну стійкість металів і сплавів в різних середовищах, внаслідок утворення в поверхневому шарі фаз складного складу і будови. В роботі досліджені фізико-механічні властивості дифузійних шарів, отриманих з використанням композиційних насичуючих середовищ. Поверхневе насичення сплавів одночасно двома елементами має перевагу в порівнянні з насиченням одним елементом. Воно дозволяє поєднувати в одержуваному покритті властивості, створені окремими елементами з особливими властивостями їх сполук. Внаслідок того, що елементи, що входять до складу насичуючої суміші, володіють різними коефіцієнтами дифузії в сплаві, а також надають взаємний вплив на швидкість дифузії один одного, вибір складу шихти при комплексному процесі є складним завданням. За результатами можна сказати, що механічні напруги (в даному випадку стискають залишкові напруги) впливають на корозійне поведінку металів, обумовлене отриманням конструкційний матеріал тим, що рівень залишкових напружень в покриттях, отриманих в композитних насичують середовищах вище. В результаті ймовірність мікровибухи пасивних оксидних оболонок зменшується, що призводить до збільшення корозійної стійкості.

Ключові слова: композиційні насичуючі середовища, латунь , дифузія, дифузійні шари, титан, алюміній, кремній, хром.

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ИССЛЕДОВАНИЕ ФИЗИКО-МЕХАНИЧЕСКИХ СВОЙСТВ ДИФФУЗИОННЫХ СЛОЕВ, ПОЛУЧЕННЫХ С ИСПОЛЬЗОВАНИЕМ КОМПОЗИЦИОННЫХ НАСЫЩАЮЩИХ СРЕД

Многокомпонентным диффузионным насыщением можно повысить твердость и износостойкость, жаростойкость и коррозионную стойкость металлов и сплавов в различных средах, вследствие образования в поверхностном слое фаз сложного состава и строения. В работе исследованы физико-механические свойства диффузионных слоев, полученных с использованием композиционных насыщающих сред. Поверхностное насыщение сплавов одновременно двумя элементами имеет преимущество по сравнению с насыщением одним элементом. Оно позволяет сочетать в получаемом покрытии свойства, создаваемые отдельными элементами с особыми свойствами их соединений. Вследствие того, что элементы, входящие в состав насыщающей смеси, обладают разными коэффициентами диффузии в сплаве, а также оказывают взаимное влияние на скорость диффузии друг друга, выбор состава шихты при комплексном процессе является сложной задачей. По результатам можно сказать, что механические напряжения (в данном случае сжимающие остаточные напряжения) влияют на коррозионное поведение металлов, обусловленное извлечением конструкционного материала тем, что уровень остаточных напряжений в покрытиях, полученных в композитных насыщающих средах выше. В результате вероятность микровзрыва пассивных оксидных оболочек уменьшается, что приводит к увеличению коррозионной стойкости.

Ключевые слова: композиционные насыщающие среды, латунь, диффузия, диффузные слои, титан, алюминий, кремний, хром.

Introduction. Composition is the main parameter that determines the choice of method and technological characteristics of the coating process, structure, layer thickness and the performance of structural materials with diffusion layers.

The grounds for choosing the composition of a single or multicomponent layer are phenomenological provisions on the choice of coating from the point of view of assessing the influence of its composition on strength characteristics, as well as an assessment of the main criteria that should be improved (increasing heat resistance, resistance in aggressive environments, etc.), and which should to study with the establishment of the laws of complex saturation [1].

Multicomponent diffusion saturation can increase the hardness and wear resistance, heat resistance and corrosion resistance of metals and alloys in various environments, due to the formation of phases of a complex composition and structure in the surface layer.

The choice of the composition of complex coatings and technologies for their preparation is a complex material science problem.

Diffusion saturation simultaneously with several elements in most cases is more effective. When combined with aluminum and silicon, the resistance is higher than when saturated with each of these elements.

The results of studies with simultaneous saturation with two elements depend on many factors and, above all, on their content in the saturating mixture, temperature and duration of the process [2, 3].

Analysis of recent research and publications. Surface saturation of alloys simultaneously with two elements has an advantage over saturation with one element. It allows you to combine in the resulting coating the properties created by individual elements with the special properties of their compounds. Due to the fact that the elements that make up the saturating mixture have different diffusion coefficients in the alloy, and also have a mutual influence on the diffusion rate of each other, the choice of the composition of the charge in a complex process is a difficult task.

Complex coatings significantly improve the surface properties of parts [4].

Establishing the general laws of structure formation of a diffusion layer during diffusion saturation with two or more elements would make it possible to predict the properties of the surface layer and designate rational CHT modes.

The simultaneous or sequential saturation of metals and alloys with several elements has so far not been sufficiently studied, especially with respect to the composition of saturating media at the same time, and sequential saturation has not been established in which saturation is necessary to ensure high performance properties. It is not completely clear which method of saturation, simultaneous or sequential, should be preferred, although the simultaneous method greatly simplifies the process of chemical-thermal treatment [5]. A significant role in the formation of coatings is played by process factors [6].

The rate of formation, the kinetics of layer growth, its structure and properties are largely determined by the process temperature, saturation time, and diffusion parameters of saturating components and significantly depend on the chemical composition, structure and properties of the material itself.

The speed of the diffusion saturation process is determined by the speed of reaching a given concentration of the diffusing element on the surface and reaching the desired depth of the diffusion layer. The speed of the process of diffusion metallization and chemical-thermal treatment is limited by the slowest stage – diffusion, ceteris paribus.

Raising the temperature is the most effective way to accelerate diffusion saturation, since the diffusion parameters and rate constants of chemical reactions are associated with temperature, an exponential dependence [7].

Improving the physicomechanical properties of aluminized and boronized parts is possible using composite saturating media, which include an exothermic chromium component (ECC). The purpose of this work is to obtain diffusion layers using composite saturating environments based on aluminum and boron using ECC.

Presenting main material. Aluminosiliconization is of interest from the point of view of studying the formation of a diffusion layer at two-component saturation. Aluminum and silicon do not form chemical compounds between themselves and there is almost no mutual solubility in the solid state. Therefore, surface doping excludes the interaction of elements in the saturating mixture, which creates favorable conditions for their diffusion into the alloy. As a result of the interaction of these elements with alloy components, complex aluminides and silicides are formed, which helps to increase the protective properties of the layer [5].

Diffusion saturation of steel with two elements (Al + Si) under conditions of fast electric heating makes it possible to significantly reduce the duration of the process, as well as to obtain better scale resistance than with diffusion saturation with one element. The process of diffusion saturation of iron and steel with aluminum and silicon is significantly accelerated in the case of electric heating.

The processes of two-component surface alloying with chromium and silicon, as well as titanium and silicon, have a technological advantage over the siliconization process. Even small additions of chromium and titanium to the saturating mixture during siliconization leads to a significant improvement in surface quality, a decrease in the porosity and brittleness of the layer, and an improvement in its adhesion to the base metal. The addition of an inert additive to the saturating mixture in an amount of 35% or more also favorably affects the surface quality of the alloy after saturation [5]. The simultaneous saturation of steel with chromium and silicon allows one to obtain diffusion layers with a complex of valuable physicochemical properties. They are more acid-resistant and scale-resistant than chrome-plated, and more plastic than siliconized.

Chromosiliconization and chromoalitization of steels increases their wear resistance, erosion and cavitation resistance, resistance to gas and electrochemical corrosion [8].

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The chromosiliconization process is carried out from powders, from pastes (coatings) [8] are used for large-sized products and, if necessary, local hardening, in melts and electrolysis with additives of a reducing agent. Gas chromosiliconization can be carried out in a chlorine medium [9].

Borosiliconization is carried out both by simultaneous and sequential saturation of metals and alloys with boron and silicon. It is used to increase wear resistance, less often heat resistance and corrosion resistance.

Carbon steel borosiliconization is carried out in powder media by gas contact method. Titanosiliconization is used to increase surface hardness, resistance to high-temperature gas corrosion and corrosion resistance in aggressive environments. The process is carried out by saturation from powder mixtures by the contact method.

Tungsten siliconization increases the wear resistance of steels under conditions of dry sliding friction and abrasive wear. However, this effect, due to the small layer thickness, is relatively small. The layers are obtained by liquid (electrolysis and without electrolysis) and metallothermal methods [8].

Obtaining diffusion layers on the steel surface using composite saturating media leads to an increase in the operational characteristics of machine parts. So aluminosiliconized layers are used to increase the heat resistance and less often the corrosion resistance of parts. It is carried out from the gas phase in powders of silicon-aluminum containing substances, from pastes and suspensions using various heating methods, from the liquid phase in melts based on aluminum and other metals, and from the gas phase.

Chromoalysis is used mainly to increase the scale and erosion resistance of parts. It is carried out from the vapor phase, the gas phase from the powders. This method significantly increases the heat resistance of carbon and alloy steel. Titanization is used mainly to increase heat resistance, corrosion resistance and wear resistance, it is carried out by the aluminothermy method of powders.

Borochroming is the process of improving the physicochemical characteristics of boride layers with high brittleness, insufficient corrosion resistance and heat resistance. Bicomponent layers are obtained by galvanometric, diffusion, combination of galvanic and diffusion methods, and surfacing [10-13].

The choice of materials is due to the possibility of studying mass steel, due to their relatively low cost, as well as the need to study the effect of carbon on the formation of the layer. As saturation activators, ammonium chloride, ammonium iodide, ammonium fluoride, and iodine were used.

Composite saturating environments (CSE) included ECC, powders: silicon, chromium, titanium, boron, aluminum and copper. The diffusion saturation process was carried out on the developed experimental industrial plant DDTU-11.

The microstructure of the structural materials with coatings based on aluminum and boron was studied on transverse sections using a Neophot – 2 microscope with an increase of x50–500. In the preparation of transverse sections, in order to prevent the destruction of coatings during processing, the samples were fixed in special clamps (steel clamps) with gaskets made of copper or aluminum foil. Processing of transverse sections was carried out according to the standard procedure [14].

After grinding is completed, subtle risks remain on the surface of the grinding. For the final leveling of the surface, the polished section was polished to a mirror shine on the cloth in the presence of an aqueous emulsion of chromium oxide (III). To show the microstructure of coatings obtained on technical iron and steels, we used a 5% alcohol solution of picric acid in ethanol [14].

Studies of the layer thickness were carried out on cylindrical samples with a diameter of 10–15 mm. The layer thickness was determined on transverse sections using a PMT – 3M instrument or a Neophot – 32 metallographic microscopes.

The study of microhardness by the thickness of the layer was measured on a PMT – 3m [15–16] by pressing a Vickers diamond tip into the material with a square base of a tetrahedral pyramid with an angle at apex 136°, which ensures a geometric and mechanical similarity of the print as it deepens indenter under the action of loading. We also used an automated microhardness-meter 402, which allows you to transfer images of automatic measurement of the fingerprint to the screen of a personal computer monitor. The surface of the measured sample before grinding microhardness was ground and polished.

The compositions of saturating environments and the characteristics of the diffusion layers formed on bra are presented in Table 1.

Table 1 The effect of the composition of the powder saturating medium on the thickness and microhardness of the formed on steel 45 at t = 1000 ºC for 2 hours.

№	Composition saturating environments,% wt.
1	22 % ЭХГ + 15% Si + 15 % Al + 2 % NH_4Cl + 2 %NaF + 2 % Cu + 32 % Al_2O_3
2	23 % ЭХГ + 17% Al + 15 % Cr + 2 % NH_4Cl + 3 % NaF + 2 % Cu + 38 % Al_2O_3
3	25 % ЭХГ + 27% Al + 18 % Ti + 3 % NH_4Cl + 3 % NaF + 2 % Cu + 22 % Al_2O_3
4	22 % ЭХГ + 15% B + 17%Si + 3 % NH_4Cl + 2% I + 2 % Cu + 49 % Al_2O_3
5	24 % ЭХГ + 17% Cr + 20 % B + 3% NH_4F +2 % NH_4I + 2 % Cu + 32 % Al_2O_3

Manganese-iron brass, designed for casting simple configuration of critical parts and armature of marine shipbuilding, operating at temperatures up to 300 °C.

Brasses intensively corrode under the influence of mineral acids (nitric, hydrochloric). Sulfuric acid acts on brass much slower, but in the presence of oxidants {$K_2Cr_2O_7$, $Fe_2(S0_4)_3$}, the corrosion rate increases by two orders of magnitude. Bars are sufficiently stable in solutions of alkalis (with the exception of ammonia) and in concentrated solutions of neutral salts.

Hydrogen sulfide provides strong corrosive action on brass. At the same time, brass with high zinc content (more than 30%) is more stable in the hydrogen sulfide medium than brass with low zinc content. For corrosion resistance research, corrosive materials are used that imitate the intended applications:

– pumps for acid transfer in the production of titanium;

– bearing units on objects of special equipment in rocket space and defense industries;

– for the manufacture of simple configuration of parts for responsible purposes and armature of marine shipbuilding, operating at temperatures up to 300 °C of massive parts, propellers and their blades.

To enhance the corrosion resistance of brass, requires a protective coating containing elements that form passive films. In this case, upon reaching the potential of ionic passivation, oxide films of the composition: Cr_2O_3, Al_2O_3,TiO_2, SiO_2 which protect the metal from destruction, are formed.

When tested in a 30% hydrochloric acid aqueous solution, covering doped with silicon and titanium have the best resistance. The metallographic analysis shows that the protective coatings in all samples were uniformly corroded to a small depth, therefore, it is advisable to use covering doped with silicon to work in a 30% hydrochloric acid solution, which, besides good corrosion resistance, also has a high wear resistance.

Conclusions. The results obtained can be explained by the formation of surfaces on the doped phases leading to surface passivation in aggressive media. It is also possible to suppose the effect of electrochemical braking of anodic dissolution of metals at a higher concentration of alloying elements compared to coatings obtained under isothermal conditions.

The growth of corrosion resistance is indicated by the surface morphology after obtaining doped protective coatings, which indicates the absence of micro-burglary.

It is known that the mechanical stresses (in this case, the compressive residual stresses) affect the corrosion behavior of metals, due to the extraction of the structural material by the fact that the level of residual stresses in coatings obtained under composite saturating environments charge is higher. As a result, the probability of micro-bursting of passive oxide skins is reduced, resulting in an increase in corrosion resistance.

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